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Multiscale modeling of organic materials

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Outlook

The work presented in this thesis enables multiple developments and extensions towards an increasingly rational approach to the design of organic materials with tailored electronic properties. In this chapter, I suggest potential future developments and extensions.

Developing Robust Structure-Property Relationships. Chapter 2 and 3 demonstrated that the use of modular coarse-graining (CGing) approaches, such as the Martini model, holds great promise for the design of organic blend morphologies aided by computer simulations. The focus on “ad-hoc” CG models in this field greatly hindered progress due to the time needed to set up and run simulations of morphologies of organic materials. The use of the Martini model, showcased in this thesis, is the most promising research direction if one wants to keep up with the rapid changes in the experimentally tested materials in this fast-paced field.

A key challenge to making efficient organic devices is determining which combination of materials and processing conditions results in a favorable morphology. The parameter space explored with the simulations of chapter 2 and 3 is only a fraction of the actual parameter space available to the studied blends. This fraction reduces to an infinitesimal amount if we consider possible variations in the chemical structures of the components of the blends. Thus, such simulations can be used to generate morphologies in order to explore more of the parameter space, striving for a high-throughput regime where

ensembles of simulations are run on high-performance computing clusters and their results distilled into robust structure-property relationships. In particular, parameters which are of high interest include: *i*) the relative miscibility of the components; *ii*) the relative abundance of configurations at the interfaces; *iii*) the mechanical properties of the blends; the *iv*) impact of the length of side chains, *v*) molecular weight, *vi*) regioregularity, *vii*) polydispersity, *etc.*, for several polymer backbone scaffolds. Moreover, regarding organic photovoltaics, the recent shift of the field from fullerene to non-fullerene³²⁶ acceptors—whose solar cells' performance now exceeds 16%³²⁷—make the latter particularly interesting systems to study.

First studies already appeared in the literature which extended the work to other important systems in organic electronics such as PEDOT:PSS.³²⁸ For future studies, the use of Martini 3²¹⁰ is recommended—already available to the scientific community via the open-beta release at <http://cgmartini.nl/index.php/martini3beta>—as, in particular, it resolves (chapter 6) the limitations found for Martini 2 concerning the description of ring structures (chapter 5), which are ubiquitous building blocks for organic semiconductors.

Extending the Simulated Solvent Evaporation Procedure. An important extension to the method developed in chapter 2 is the inclusion of interfaces between the organic film and 1) the *substrate* on top of which thin films are solution-processed, and 2) the *vapor phase* which is present experimentally. This would allow a more realistic description of the evaporation process, and, more importantly, would give access to two critical observables which can be compared to experiments: 1) the organization of the molecules along the direction normal to the substrate plane, that is, the vertical organization of the blend: for some systems, an enrichment in one of the components is observed towards the film-substrate or film-vapor interface;³²⁹ 2) the preferential orientation, *e.g.*, face-on or edge-on, of the π -system of the components with respect to the substrate: this orientation can greatly affect device properties such as charge transport.³³⁰ Negi *et al.* recently pioneered the inclusion of such interfaces in a CG molecular dynamics approach to simulate the solution-processing of polymer-fullerene blends.³³¹ The method would benefit from a combination with the Martini force field, to go beyond the necessary constant re-parametrization of the non-transferable CG models^{108,331} used in the work.

A Wealth of Morphologies. Chapter 4 gave only a flavor of the avenues opened by the availability of the morphologies generated with the simulated processing protocols described in chapter 2. We have seen that the direct retrieval of atomistic detail is possible through established backmapping procedures,²⁹ opening the way for improved quantum mechanical calculations which can fully benefit from large-scale derived structural information. The large-scale structural information can also be used in so-called quantum chemical Monte Carlo (QCMC) methods used to simulate charge transport in organic devices.³³² QCMC methods, in order to predict the behavior of a system based

on statistical rules, require an atomistic description of the system within which charge transport will occur. This differentiates them from Kinetic MC approaches, where the description of the morphology and electronic couplings is simplified.³³² Backmapped morphologies such as the ones developed in this work can be used to introduce an explicit link between the molecular-scale and the device-scale. Besides the morphological details, electronic couplings relevant to charge transport can be explicitly computed given the atomic resolution of the morphology.

The microscopic, atom-resolved information on the donor-acceptor configurations (chapter 4) makes it possible to compute a number of other interesting electronic properties which are relevant to the functioning of organic devices. In particular, charge-transfer states are particularly relevant for the functioning of organic solar cells. A comprehensive three-dimensional charge-transfer state energy landscape could be obtained from the backmapped morphologies of chapter 4. This would go beyond strictly model-like^{70,233} donor-acceptor interfaces, possibly bringing insights on the charge separation mechanism crucial to the functioning of organic solar cells. Another interesting property is the computation of non-radiative recombination rates, which are responsible for voltage losses in organic solar cells.²³⁴ Such rates have been found to depend on the relative orientation of donor and acceptor molecules at their interface.³³³ The morphologies allow for state-of-the-art prediction of the relative abundance of specific donor-acceptor configurations—which can largely affect such rates^{234,333}—a necessary step in the direction of an increased rational approach to the design of high performance organic solar cells. Of particular interest is the comparison of such electronic properties as a function of structural features between fullerene and non-fullerene acceptors,³²⁶ as the anisotropic shape of (most) non-fullerene acceptors is expected to affect significantly their packing in organic blends. For all these proposed studies, the fact that the underlying morphologies are obtained via large-scale simulations which account for fabrication conditions means that the various electronic processes can also be studied as a function of such conditions.

Future of Martini. The realization of the limitations of Martini 2 described in chapter 5 led to the development of Martini 3.²¹⁰ Along with recent promising works applying Martini to organic materials (chapters 2–4 and Refs. 266,267,328), the newly developed parametrization of ring structures in particular (chapter 6) is expected to boost the application of Martini in soft materials science. This is moreover desirable so as to stress-test the parametrization in this relatively new area of application of the model.

To this end, tools to automate mappings, determination of bonded parameters, and bead assignments would be of great importance to accelerate the building of models for the new molecules which come out every week from the many labs around the world in search of organic materials with improved performances. Thus, efforts such as Martinize 2³³⁴—a tool aimed at producing CG models from atomistic structures—or Automartini²⁷⁹ or Cartographer³⁰²—tools for automated atomistic-to-CG mappings—are most welcome.

